

09/890967

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SUGHRUE MION ZINN MACPEAK & SEAS, PLLC

August 8, 2001

BOX PCTCommissioner for Patents
Washington, D.C. 20231TE
PCT/AH00/00018
-filed February 8, 2000Re: Application of **Jeremy Denis GLENNON** and **John Harris STEPHEN****COMPLEXING AGENTS**Assignee: **UNIVERSITY COLLEGE CORK**
Our Ref: **Q65804**

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

- an English translation of the International Application.
- a Preliminary Amendment

The Declaration and Power of Attorney and executed Assignment with PTO Form 1595 will be submitted at a later date.

It is assumed that copies of the International Application, the International Search Report and copies of each reference cited therein, the International Preliminary Examination Report, and priority document will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

Please see attached preliminary amendment before calculating Government filing fee.

The Government filing fee is calculated as follows:

Total claims	<u>18</u>	-	<u>20</u>	=	<u>0</u>	x \$18.00 =	<u>\$0.00</u>
Independent claims	<u>1</u>	-	<u>3</u>	=	<u>0</u>	x \$80.00 =	<u>\$0.00</u>
Base Fee							<u>\$860.00</u>
TOTAL FEE							<u>\$860.00</u>

A check for the statutory filing fee of \$860.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.



SUGHRUE MION ZINN MACPEAK & SEAS, PLLC

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JC05 Rec'd PCT/PTO 08 AUG 2001

Entering National Stage of PCT/IE00/00018

Attorney Docket Q65804

Page 2

Priority is claimed from February 8, 1999 based on Irish Application No. S990086.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Robert V. Sloan".

Robert V. Sloan

Registration No. 22,775

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Date: August 8, 2001

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of PCT/IE00/00018

Jeremy Denis GLENNON, et al. Attorney Docket Q65804

Appln. No.: Not yet assigned Group Art Unit: Not yet assigned

Confirmation No.: not yet assigned Examiner: Not yet assigned

Filed: August 8, 2001

For: COMPLEXING AGENTS

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-identified application as follows:

IN THE SPECIFICATION:

The specification is changed as follows:

Page 1, after the title insert the heading

BACKGROUND OF THE INVENTION

Page 5, after line 7, insert the heading

SUMMARY OF THE INVENTION

Page 10, line 14 insert the heading

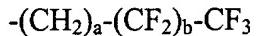
DETAILED DESCRIPTION OF THE INVENTION

PRELIMINARY AMENDMENT
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IN THE CLAIMS:

Please enter the following amended claims:

3. (Amended) A thiourea according to claim 1 wherein R² is

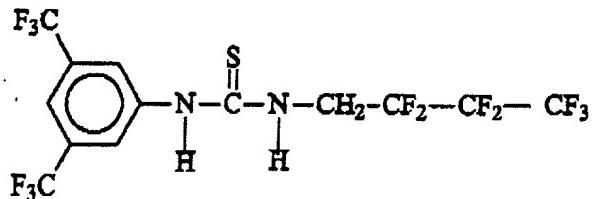


wherein a is an integer not less than 1 and b is a whole number from 0 to 6.

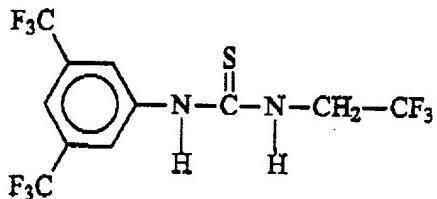
7. (Amended) A thiourea according to claim 1 wherein R³ is H.

8. (Amended) A thiourea according to claim 1 wherein R⁴ is H.

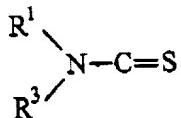
9. (Amended) A thiourea according to claim 2, viz. one of formula



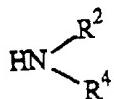
10. (Amended) A thiourea according to claim 2, viz. one of formula



11. (Amended) A method of producing a substituted thiourea of the formula given and defined in claim 1, characterized by reacting a compound of general formula



with a compound of general formula



wherein R¹, R², R³ and R⁴ are as defined in any said claim.

12. (Amended) A method of extracting a noble metal from a matrix, said method characterised in treating a matrix with a substituted thiourea according to claim 1, and subjecting the thus treated matrix to supercritical fluid extraction.
14. (Amended) A method according to claim 12 wherein the superficial fluid is liquid carbon dioxide.
15. (Amended) A method according to claim 12 wherein the treatment with substituted thiourea is performed in the presence of an oxidant.
17. (Amended) A method according to claim 12 wherein the treatment and extraction are carried out at room temperature and are followed by recrystallisation of the product from petroleum ether (100-200°).
18. (Amended) Use of a thiourea according to claim 1 in the extraction of gold, platinum, silver, palladium or rhodium from a matrix.

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REMARKS

The above specification has been amended to add section headings to the various sections of the application and to delete the multiple dependencies therein. Entry and consideration of this Amendment and an early and favorable action on the merits are respectfully requested.

Respectfully submitted,



Robert V. Sloan
Registration No. 22,775

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APPENDIX

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

The specification is changed as follows:

Page 1, after the title insert the heading

BACKGROUND OF THE INVENTION

Page 5, after line 7, insert the heading

SUMMARY OF THE INVENTION

Page 10, line 14 insert the heading

DETAILED DESCRIPTION OF THE INVENTION

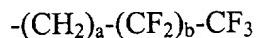
IN THE CLAIMS:

Delete the heading “Claims” and insert the heading

WHAT IS CLAIMED IS:

The claims are amended as follows:

3. (Amended) A thiourea according to Claim 1 or 2 wherein R² is



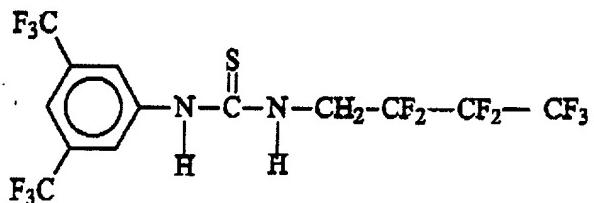
wherein a is an integer not less than 1 and b is a whole number from 0 to 6.

7. (Amended) A thiourea according to any preceding claim 1 wherein R³ is H.

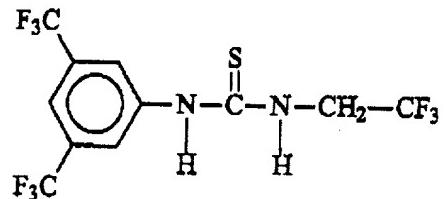
8. (Amended) A thiourea according to any preceding claim 1 wherein R⁴ is H.

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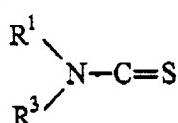
9. (Amended) A thiourea according to ~~Claims 2, 4, 7 and 8~~, viz. one of formula



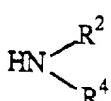
10. (Amended) A thiourea according to ~~Claims 2, 5, 7 and 8~~, viz. one of formula



11. (Amended) A method of producing a substituted thiourea of the formula given and defined in ~~any preceding claim 1~~, characterized by reacting a compound of general formula



with a compound of general formula



wherein R¹, R², R³ and R⁴ are as defined in any said claim.

PRELIMINARY AMENDMENT

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12. (Amended) A method of extracting a noble metal from a matrix, said method characterised in treating a matrix with a substituted thiourea according to any of Claims 1-to-10, and subjecting the thus treated matrix to supercritical fluid extraction.
14. (Amended) A method according to Claim 12-or-13 wherein the superficial fluid is liquid carbon dioxide.
15. (Amended) A method according to any of Claims 12-to-14 wherein the treatment with substituted thiourea is performed in the presence of an oxidant.
17. (Amended) A method according to any of Claims 12-to-16 wherein the treatment and extraction are carried out at room temperature and are followed by recrystallisation of the product from petroleum ether (100-200°).
18. (Amended) Use of a thiourea according to any of Claims 1-to-10 in the extraction of gold, platinum, silver, palladium or rhodium from a matrix.

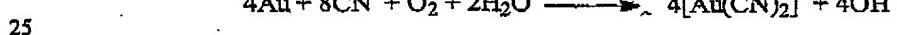
"Complexing Agents"

This invention relates to a complexing agent and in particular to new fluorinated thiourea complexing agents and fluorinated thiourea complexing agents for use in the extraction of noble metals such as gold, platinum, silver, palladium and rhodium.

Complexing agents are widely employed in the extraction and recovery of metals such as gold, platinum, silver, palladium and rhodium.

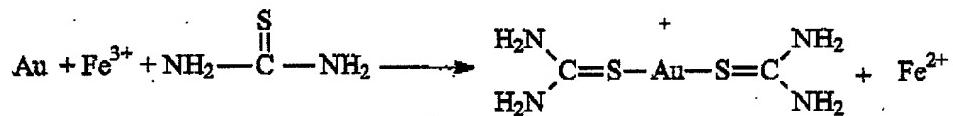
10 For example, gold is a soft yellow metal having a melting point of 1063°C with the highest ductility and malleability of any element. It is chemically unreactive and is not attacked by oxygen or sulphur but reacts readily with halogens or with solutions containing or generating chlorine such as "aqua regia". Its most common compounds exist in the (I) and (III) oxidation states.

15 Heretofore, the extraction of gold from ore and from other solid phases such as in solid phase extraction has been commonly carried out by using cyanide or thiourea as reagents. In the most commercially important method for gold extraction finely crushed ore is treated with sodium cyanide in the presence of oxygen to give a sodium gold cyanide complex, which is typically absorbed onto activated carbon. The sodium gold cyanide complex can be re-extracted later and reduced to the metal, (H. Schmidbaur, Interdisciplinary Science Reviews, 17 (3), 213, 1992 and A. Sigel and H. Sigel in "Handbook on Metals in Clinical and Analytical Chemistry", Ed. H.G. Seiler, 1994 p388) viz:



However, treatment with sodium cyanide is environmentally unfriendly while the efficiency of the reaction can be poor and variable according to the ore type. Accordingly, other methods of gold and silver extraction have been developed e.g. thiourea-based extraction. Thiourea-based extractions enjoy the advantages of higher leaching efficiency, rapid leaching, adaptation to a variety of refractory ores and reduced toxicity to the environment. Accordingly, thiourea is an attractive procedure for the extraction of both gold and silver.

For example, it has been demonstrated (C.K. Chen, T.N. Lung and C.C. Wan, *Hydrometallurgy*, 5, 207, 1980) that employing Fe^{3+} as oxidant in acid solutions resulted in leaching with thiourea which was ten times faster than leaching with sodium cyanide, *viz.*:



15

However, excessive consumption of thiourea in the process has limited its industrial application.

Various attempts have been made to reduce thiourea consumption. For example, in order to reduce thiourea consumption in gold extraction it has been suggested (C.C. Kenna, *Gold Bull.*, 24(4), 126, 1991) that the complexing of ferric ions could be utilised in reducing their oxidative power to a level where oxidation of gold still proceeded at an acceptable rate while oxidation (and consumption) of thiourea was greatly reduced.

U.S. Patent Specification No. 5126038 also discloses that alkyl hydroxamic acids or their salts may be used to improve extraction of precious metals, including gold, from sulphide ores in combination with standard sulphide ore collectors such as xanthates, substituted thioureas and the like.

5

G. Zuo and M. Muhammed, Separation Science and Technology, 25(13-15), 1785, 1990 also describe the synthesis and characterisation of a family of thiourea based reagents for the extraction of Au(III) and Ag(I) ions through complex formation from HCl solutions and also disclose the synthesis of several co-ordinating polymers by grafting thiourea functional groups onto commercial macroporous polystyrene polymer matrices.

In order to avoid the use of thioureas, azacrowns have also been used to facilitate transport of $\text{NaAu}(\text{CN})_2$ into an organic phase from an aqueous phase (M. Tromp, M. Burgard, M.J.F. Leroy and M. Prevost, J. of Membrane Science, 38, 295, 1988). In addition, Izatt et al., (R.L. Bruening, B.J. Tarbet, T.E. Krakowiak, M.L. Bruening, R.M. Izatt and J.S. Bradshaw, Anal. Chem., 63(10), 1014, 1991 and R.L. Bruening, B.J. Tarbet, K.E. Krakowiak, R.M. Izatt and J.S. Bradshaw, J. Heterocyclic Chem., 27, 347, 1990) have developed silica gel bound thia-macrocycles which have shown high selectivity for Au(III).

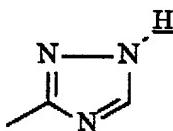
Supercritical fluid extraction (SFE) has developed into an attractive alternative to conventional solvent extraction to recover organic compounds from solids in particular. A useful fluid for SFE work is liquid carbon dioxide due to its moderate critical constants

($T_c = 31.1 \text{ }^\circ\text{C}$, $P_c = 72.8 \text{ atm}$), inertness, ease of availability, low cost and ease of final removal. However, direct extraction of metal ions by supercritical CO_2 is very inefficient due to the charge neutralisation required and weak solute-solvent interactions.

5

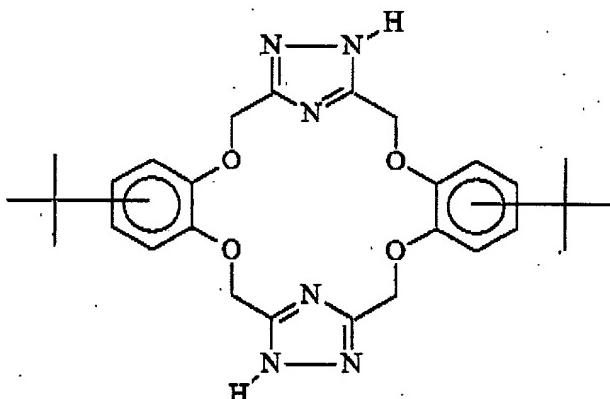
Supercritical fluid extraction of gold has been described by S. Wang, S. Elshani and C.M. Wai, Anal. Chem., 67, 919 1995 where $\text{Au}(\text{III})$ ions were extracted by bis-triazolocrowns from wet solid matrices using supercritical CO_2 modified with methanol. Neutral gold complexes were formed due to the presence of triazolo protons:

10



which were soluble in modified SF-CO_2 . The presence of the triazolo protons was necessary for the extraction of the metal ions to give a neutral metal ion-ligand complex:

15



and no extraction was possible without methanol modifier or water in the solid phase. Supercritical CO₂ has also been utilised (E.O. Out, Separation Science and Technology 32.6, 1107, 1997) to elute gold in the form of NaAu(CN)₂ previously adsorbed on activated charcoal employing tributylphosphate to facilitate charge neutralisation. However, the presence of water in the solid phase was required for the extraction while as indicated previously the use of cyanide is undesirable for environmental and safety reasons.

An object of the invention is to overcome the problems of the prior art.

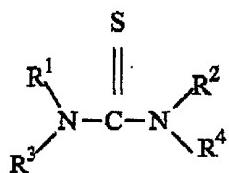
10

A further object of the invention is to provide a complexing agent or ligand for noble metal (including gold) extraction.

15

A still further object of the invention is to provide a method for extracting noble metals (including gold) which overcomes the problems of the prior art.

According to the invention there is provided a thiourea having the general formula:



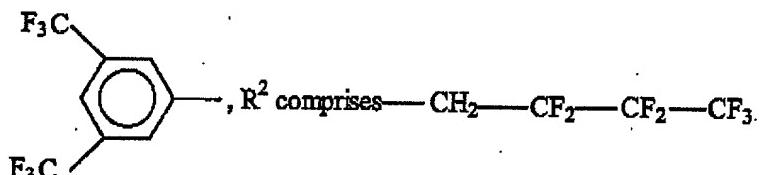
20 wherein each of R¹ and R² independently comprises an alkyl, alkaryl or aryl group or a substituted derivative thereof, and contains at least one fluorine atom, and wherein each of R³ and R⁴ is selected from the group which consists of H, alkyl, alkaryl and

DEPARTMENT OF TRADE AND INDUSTRY
PATENT OFFICE

aryl, and substituted derivatives thereof, including fluorine - containing derivatives. In one aspect of the invention R³ and R⁴ are selected from the group consisting of alkyl, alkaryl and aryl, and substituted derivatives thereof including fluorine - containing derivatives. The fluorinated derivatives of the invention are extremely useful for

5 analytical assays for the determination of gold levels, and for gold recovery, as well as for determination of platinum, silver, palladium and rhodium levels and for their recovery.

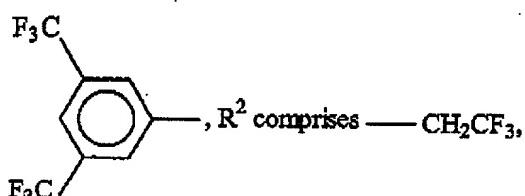
Preferably, R¹ comprises



R³ comprises H and R⁴ comprises H.

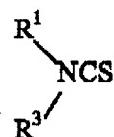
Alternatively, R¹ comprises

15

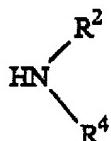


R³ comprises H and R⁴ comprises H.

The invention also extends to a method of producing a fluorinated thiourea comprising reacting a compound of general formula

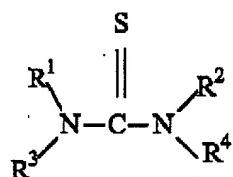


5 with a compound of general formula



where both R^1 and R^2 contain fluorine.

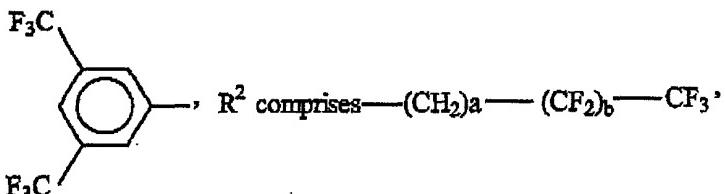
The invention also relates to a method for extracting gold from a matrix comprising
10 treating the matrix with a thiourea having the general formula



where R^1 and R^2 comprise a fluorine containing alkyl, alkaryl, aryl or substituted derivatives thereof and R^3 and R^4 are selected from the group comprising H, alkyl, aryl
15 or substituted derivatives thereof and subjecting the matrix to supercritical fluid extraction (SFE).

Preferably, the supercritical fluid used in the extraction comprises liquid carbon dioxide.

Preferably, R¹ comprises



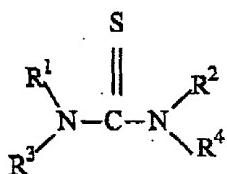
R³ comprises H and R⁴ comprises H where a ≥ 1 and b = 0 – 6.

In one embodiment of the invention the gold is extracted in the presence of an oxidant.

- 10 Suitably, the oxidant comprises Fe (III) ions.

Advantageously, b > 3, i.e. b = 4, 5 or 6.

The invention also extends to the use of a fluorinated thiourea of the general formula

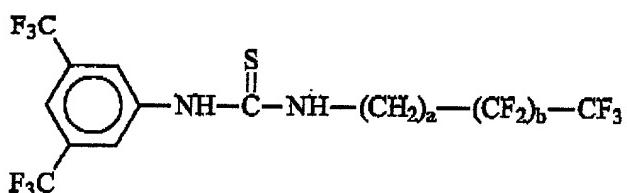


where R¹ and R² comprise a fluorine containing alkyl, alkaryl, aryl or substituted derivatives thereof and R³ and R⁴ are selected from the group comprising H, alkyl, aryl,

alkaryl or substituted derivatives thereof in the extraction of a noble metal, including gold, platinum, silver, palladium and rhodium from a matrix.

Surprisingly, it has been found that fluorinated thioureas of the general formula:

5



wherein $a \geq 1$ and $b = 0 - 6$

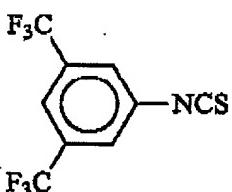
efficiently extract Au(I) and Au(III) from a solid matrix in unmodified supercritical CO₂ 10 and furthermore may extract gold from a solid containing gold in its elemental form in the presence of an oxidant. Fe(III) ions are particularly suitable as oxidants. The addition of modifiers or protons is not required and extraction can be carried out using fluorinated thioureas alone.

15 In contradistinction, thiourea itself does not form a neutral complex with gold. It forms Au [SC(NH₂)₂]₂⁺.

In a preferred embodiment of the invention $b > 3$, i.e. $b = 4, 5$ or 6 .

20 The fluorinated thioureas of the invention have a high solubility in supercritical CO₂ and are extremely efficient at solubilising and carrying noble metals such as gold for the purposes of extraction, recovery, deposition or impregnation.

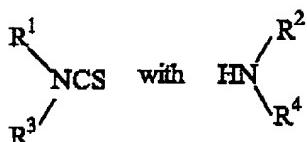
The fluorinated thioureas can be synthesised in a simple one-step process by the reaction of:



5

with the appropriate amine $\text{NH}_2\text{CH}_2(\text{CF}_2)_b\text{CF}_3$ where $b = 0$ or 2 to 6 in a room temperature (exothermic) reaction and recrystallisation from petroleum ether (100-120) to give colourless products in 62 to 81% yields.

10 The compositions of the invention can therefore be formed by the simple reaction of:

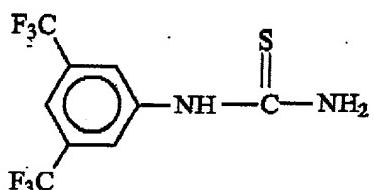


where both R^1 and R^2 contain fluorine.

15 Various embodiments of the invention will now be described by way of Example only, having regard to the following data and examples.

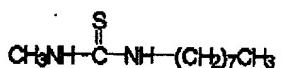
Comparative Examples

(a)



The aforementioned fluorinated thiourea is known from the prior art and is
5 commercially available from FLUOROCHEM.

(b)



- 10 In a round bottom flask 6.45g (0.05 mole) of octyl-1-amine was added to 3.65g (0.05 mole) melted methyl isothiocyanate, with stirring, under nitrogen in an ice bath. A rapid exothermic reaction ensued and the reaction was allowed to reach room temperature overnight. The colourless solid product (10.02g, 99% yield) was recrystallised from 100-120°C petroleum ether to give 9.99g of N-methyl,N'-octyl thiourea as a white solid.
15 Note: The oil, which settles out on cooling, solidifies on standing, yield 99%.

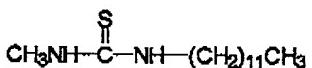
Elemental Analysis for C₁₀H₂₂N₂S

Calculated: C: 59.36, H: 10.96, N: 13.84, S: 15.84%

Found: C: 59.60, H 10.99, N: 13.50, S: 16.11%

(c)

20



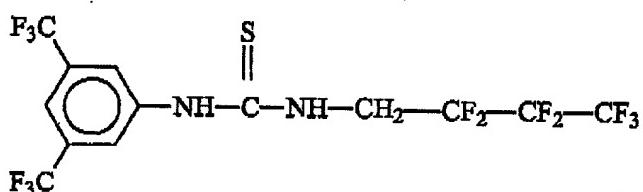
In a round bottom flask 9.27g (0.05 mole) dodecyl-1-amine was added to 3.65g (0.05 mole) of melted methyl-isothiocyanate with stirring under nitrogen. A rapid exothermic reaction ensued and the reaction mixture was allowed to reach room temperature overnight. The colourless solid product 12.45g (96% yield) was recrystallised from 100-
 5 120°C petroleum ether to give 12.27g (95% yield) of N-methyl, N'-dodecyl thiourea as white crystals.

Elemental Analysis for C₁₄H₃₀N₂S

Calculated: C: 65.05, H: 11.70, N: 10.84, S: 12.40%

Found: C: 64.90, H: 11.67, N: 11.10, S: 12.78%

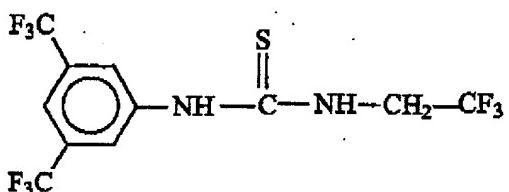
10 Example 1



To 0.518 g (0.0026mole) 1H, 1H-heptafluorobutylamine (Fluorochem (Trade Mark)
 15 Product FO4396) in a round bottom flask was added 0.705g (0.0026mole) 3,5-di(trifluoromethyl) phenylisothiocyanate (Fluorochem (Trade Mark) Product F03115B). After stirring for one minute the miscible liquids solidified to a colourless solid in an exothermic reaction. After the reaction mixture had cooled it was allowed to stand for 1 hour at room temperature and the product was recrystallised from petroleum ether
 20 (100-120) to give 0.972 g of pure product (80% yield) as colourless crystals, mp 130-132°C.

Elemental Analysis for C₁₅H₁₇N₂SF₁₃:

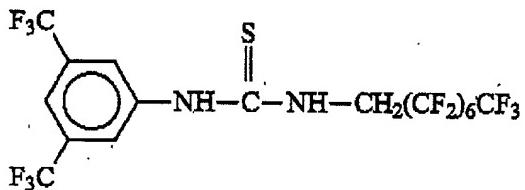
Calculated: C: 33.20, H: 1.50, N: 5.96, Found C: 33.05, H: 1.49, N: 6.12%

Example 2

5

- To 0.705g (0.0026 mole) 3,5-di(trifluoromethyl)-phenylisothiocyanate in a round bottom flask cooled in an ice bath, with stirring under nitrogen, was added 0.281g (0.00283 mole) trifluoroethyl amine (Aldrich (Trade Mark) product 26,904-2). After a short period an exothermic reaction occurred to give a colourless solid. The reaction mixture was then allowed to warm to room temperature and was left for 1 hour under a stream of dry nitrogen to remove excess volatile amine (bp 36°C). The solid was recrystallised from petroleum ether (100-120) to give a pure product as fluffy colourless crystals 0.60g (62% yield), m.p. 133-136 °C.
10. Elemental Analysis for C₁₁H₇N₂SF₉:

15. Calculated: C: 35.64, H: 2.04, N: 7.55, Found C: 35.94, H: 2.20, N: 7.73%

Example 3 (a)

- To 3.28 (0.0121 mole) 3,5-di(trifluoromethyl) – phenylisothiocyanate in a round bottom flask was added 4.82g (0.0121 mole) 1H, 1H – perfluoro-octylamine Lancaster (Trade

Mark) product 16845 with stirring. An exothermic reaction rapidly ensued and after cooling to room temperature was allowed to remain for 2 hours. The white solid product was recrystallised from 100-120°C petroleum ether to give 6.50g pure product (81% yield) as a colorless crystalline solid.

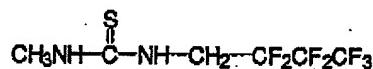
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Elemental Analysis: C₁₇H₁₇N₂SF₂₁

Calculated: C:30.46, H:1.05, N:4.18; Found: C:30.60, H:1.16, N:4.40%

Example 3 (b)

10



In a round bottomed flask 5.92g (0.03 mole) of 1H, 1H- heptafluorobutyl amine was added to 2.18g (0.30 mole) of melted methyl-isothiocyanate with stirring under nitrogen. An exothermic reaction ensued and the reaction mixture was allowed to reach room temperature overnight. The colourless product 8.10g (100% yield) was recrystallised from 100-120°C petroleum ether to give N-methyl, N'-heptafluorobutyl thiourea, 6.91g, as a white solid in 85% yield.

Elemental Analysis for C₈H₁₇N₂SF₇:
 Calculated: C: 26.48, H: 2.59, N: 10.29, S: 11.78%
 Found: C: 26.71, H: 2.67, N: 10.50, S: 12.25%

Example 4

The solubility of the ligand of the comparative Examples (a)-(c) in supercritical CO₂ was compared with the solubilities of the ligands of Examples 1 and 2 and 3 in supercritical CO₂.

In each case, a weighed amount of the ligand of the respective comparative Example of approximately 60 mg was placed in a glass tube (2cm x 0.5cm i.d.) and plugged with glass wool at both ends. The glass tube was placed inside the extraction vessel and statically extracted for 30 minutes. The inlet valve for SF-CO₂ was then closed and the outlet valve opened into a collecting solution. The loss of weight of the glass tube after SFE corresponded to the solubility of the ligand in 2.2 ml 100% SF-CO₂. The procedure was carried out at 60°C and two different pressures namely 200 and 300 atmospheres.

- 5 In all three cases, most of the ligand appeared to remain in the glass tube indicating poor solubility in SF-CO₂.

Solubility of the ligand of Example 1 in supercritical CO₂:

- The procedure outlined above in Example 4 was repeated for the ligand of Example 1.
10 This time none of the ligand remained in the glass tube, indicating excellent solubility in SF-CO₂ at both pressures.

Solubility of the ligand of Example 2 in supercritical CO₂:

- The procedure outlined above in Example 4 was repeated for the ligand of Example 2.
15 Again, none of the ligand remained in the glass tube, indicating excellent solubility in SF-CO₂ at both pressures.

Solubility of the ligand of Example 3(a) in supercritical CO₂:

- The procedure outlined above in Example 4 was repeated for the ligand of Example
20 3(a).

Again, none of the ligand remained in the glass tube, indicating excellent solubility in SF-CO₂ at both pressures.

Solubility of the ligand of Example 3(b) in supercritical CO₂:

- 5 The procedure outlined above in Example 4 was repeated for the ligand of Example 3(b).

Again, none of the ligand remained in the glass tube, indicating excellent solubility in SF-CO₂ at both pressures. Larger amounts of ligand 3(b) were used and solubilities in excess of 0.7 M were thus found at both pressures.

- 10 Thus the newly synthesised thioureas were found to be highly soluble in supercritical CO₂ compared to the fluorinated and two non-fluorinated thioureas of the Comparative Examples (a)-(c).

- A number of experiments were carried out to demonstrate the extraction efficiencies of
15 the fluorinated thioureas of the invention.

Example 5 (a) (comparative): Supercritical Fluid Extraction of Au(III) as AuCl₄ using the compound of the comparative Example (a).

- 20 Gold Au(III) extraction by the ligand of the comparative Example (a) was investigated employing a BDH Gold (III) standard containing 1000 ppm Au(III) (aqueous AuCl₄). Thus 60 µl of solution Au(III) containing 3.05×10^{-7} moles Au(III) was applied to a 3cm diameter filter paper. The filter paper was allowed to dry and then placed in a glass tube (2cm x 0.5cm i.d.), plugged with glass wool at both ends. 20mg of ligand of the
25 comparative Example (a) (in excess of over 200 fold over Au(III) level) was then placed

in the same glass tube and plugged with glass wool. The temperature of the extraction vessel was then set at 60°C and the pressure was varied as indicated in Table 1.

The extraction vessel was statically extracted for 20 minutes and then dynamically
 5 extracted into a collecting solvent of 4 ml methanol for 15 minutes (0.8 ml CO₂/minute flow rate). The methanol solution was then made up to 10 ml using additional methanol. Levels of gold in solution were then determined by atomic absorption spectroscopy. The procedure was carried out at different pressures from 200-400 atm.
 The following extraction percentages were obtained:

10

TABLE 1

	Pressure SF-CO ₂ (atm)	Atomic Absorption (A.U.)*	Extraction (%)
15	200	0.000	0
	250	0.000	0
	300	0.001	~ 0.0
	350	0.000	0
	400	0.024	6.7

20 * The % extraction is calculated with reference to the Atomic Absorption reading obtained for 10ml of collecting solution spiked directly with 60µl of the 1000ppm Au(III) standard. (For example for the data presented in Table 1 a standard of 60 µg/10 ml = 6ppm Au, gave an absorption value of 0.359, representing 100% extraction. Note: such recordings of standard values were carried out alongside the sample analysed on
 25 the same day.)

400 atm was the only pressure of SF-CO₂ to give detectable Au(III) extraction. In all runs most of the ligand appeared to remain in the glass tube indicating poor solubility in SF-CO₂.

5

Example 5 (b) (comparative): Supercritical Fluid Extraction of Au(III) as AuCl₄⁻ using the compound of the comparative Example (b).

The procedure of Example 5(a) was repeated for Comparative Example (b) to give 3.2% gold extraction at 250 atmospheres and 2.0% at 450 atmospheres pressure.

- 10 Most of the ligand appeared to remain in the glass tube after all runs indicating poor solubility in SF-CO₂

Example 5 (c) (comparative): Supercritical Fluid Extraction of Au(III) as AuCl₄⁻ using the compound of the comparative Example (c).

- 15 The procedure of Example 5(a) was repeated for Comparative Example (c) to give 2.6% gold extraction at 250 atmospheres and 1.3% at 450 atmospheres pressure.
Most of the ligand appeared to remain in the glass tube after all runs indicating poor solubility in SF-CO₂

- 20 Example 6 (comparative)

The procedure in Example 5(a) was repeated except the temperature of the extraction procedure was varied from 60-120°C, while maintaining the pressure of the extractor at 400 atm. The following results were obtained:

19

TABLE 2

Temperature (°C)	Atomic Absorption (A.U.)*	Extraction (%)
5		
60	0.027	8.8
80	0.002	0.7
100	0.006	2.0
120	0.005	1.6
10		

* A standard of 6ppm Au, gave an absorption value of 0.305 = 100%

The % extraction of gold remained low.

15 Example 7

The procedure in Example 6 was repeated with the ligand from Example 1 being used in place of the ligand of the Comparative Example (a). The following % extraction values were obtained at differing pressures for extraction of Au(III):

20

25

TABLE 3

	Pressure SF-CO ₂ (atm)	Extraction (%)
5	200	61.2
	250	92.7
	300	83.7
	350	75.3
	400	78.1

Percentage extraction with the ligand of the invention was therefore excellent at 92.7% compared with the poor extraction (<10%) with the ligands of the comparative Examples.

Example 8

Reduction of Au(III) to Au(0) was accomplished by treatment with hydroxylamine hydrochloride followed by sodium hydroxide.

The procedure in Example 7 was repeated except the conditions were altered to 60°C at 250 atm. The 60µl of AuCl₄⁻ was replaced by 60µl of a well mixed even suspension of Au(0) applied to the filter paper which was allowed to dry to give a black-blue colour.

The collected methanol solutions, made up to 10 ml as before, were analysed by Atomic Absorption Spectroscopy as before, giving the following % extraction values:

TABLE 4

5	Pressure SF-CO ₂	Atomic Absorption	Extraction
	(atm)	(A.U)*	(%)
10	200	0.001	~ 0.0
	250	0.002	~ 0.0
	300	0.0001	~ 0.0
	350	0.002	~ 0.0
	400	0.002	~ 0.0

15

Accordingly, the ligand of Example 1 did not extract Au(0). Moreover, at the end of the runs the blue-black colour of Au(0) remained on the filter paper and no ligand remained in the tube. However, as described further below the gold could be extracted following oxidation of Au(0) to either Au(I) or Au(II).

20

Example 9

The procedure in Example 8 was repeated but 40mg of solid Au(0) was used in place of the Au(0) suspension deposited on the filter paper to give an identical result to Example 8.

25

Example 10

The procedure of Example 9 was repeated utilising 20 mg of the ligand Example 1 except 11.2 mg of solid Au(0) was used and on two occasions the Au(0) was first oxidised to Au(I) by spiking 60 µl of Fe(III) (1000 ppm stock solution) onto the solid 5 Au(0) directly and then allowed to dry. In the case where Fe(III) had been added when the collected methanol solution (as usual made up to 10 ml) was analysed by atomic absorption a large signal was obtained (0.252) and (0.253) indicating extraction of Au(I). Fe(III) was the limiting reagent as:



and therefore 60µl 1000ppm Fe(III) (1.075µmole) is equivalent to 212µl of 1000ppm Au(I) (0.2 mg Au).

15 Table 5 below outlines the results obtained following application of Fe(III):

20

25

30

35

TABLE 5

	Sample	Atomic Absorption	Extraction
		(A.U.)*	(%)
5	11.2mg Au(0)	0.001	0
	+ 20mg ligand of Example 1		
10	11.2 mg Au(0)	0.252	20.0
	+ 60 µl Fe(III) + 20mg ligand of Example 1		
15	11.2 mg Au(0)	0.253	20.0
	+ 60 µl Fe(III) + 20mg ligand of Example 1		

A 212µl aliquot of 1000 pp, Au(III) standard solution gave an absorption value of 1.263
 20 = 100%.

Accordingly, Au(0) has been successfully oxidised by Fe(III) to give Au(I) which has been extracted with the fluorinated ligand of the invention. That only 20% of the theoretically freed gold (by Fe) was finally detected by atomic absorption is not surprising in view of the fact that the Fe(III) was applied as a 1000ppm aqueous nitrate solution to the solid Au(0) on the filter paper without thorough mixing.

Nevertheless, the method can be employed successfully as a qualitative test for Au(0).

Example 11

- 5 The procedure of Example 7 was repeated employing the ligand of Example 2 in place
of the ligand of Example 1 and utilising 50 μ l Au(III) standard solution in place of 60 μ l to
give the following % extraction results at differing pressures of SF-CO₂ at 60°C.

TABLE 6

10	Atmosphere SF-CO ₂	Extraction
15		(%)
	200	41
	250	51
	300	22
	400	14

20

Example 12

- The procedure of Example 11 was repeated except Au(III) standard was replaced by
5.7 mg solid Au(0) and extraction was determined under previously optimised
25 conditions 60°C/250 atm SF-CO₂. Table 7 summarises the results:

TABLE 7

5	Sample	Extraction
		(%)
10	Au(O) + ligand	~ 3

Example 13

- 15 Above Example 12 was repeated except that 30µl 1000 ppm Fe(III) standard (aqueous nitrate) was spiked onto the Au(0) prior to extraction with SF-CO₂ (250atm/60°C). Table 8 below summarises the results obtained.

TABLE 8

20	Sample	Extraction
		(%)
25	Au(O) + 30µl Fe(III) + 20mg ligand	57

30

The above percentage is based on the Fe(III) oxidisable quality of gold i.e. Fe(III) is the limiting reagent.

- 35 57% of the "freed" gold Au(I) was therefore extracted with the fluorinated ligand of the invention.

Advantages of the invention include (but are not limited to) the following:

The linear fluorinated thioureas of the invention therefore have the unexpected property
5 of extracting Au(III) in supercritical CO₂. In addition Au(I) may be extracted from Au(0)
(in its elemental state) by prior treatment with Fe(III).

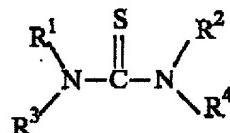
The complexing agents and extraction methods of the invention are highly efficient and
do not require the use of cyanides. In addition, the fluorinated thioureas of the
10 invention facilitate the extraction of noble metals (including gold, platinum, silver,
palladium and rhodium) without excessive thiourea consumption.

Moreover, extraction of noble metals (including gold, platinum, silver, palladium and
rhodium) using fluorinated thioureas and supercritical fluid can be effected without
15 requiring the addition of modifiers, protons and the like.

The invention is not limited to the embodiments herein described which may be varied
in construction and detail.

Claims

1. A substituted thiourea having the general formula

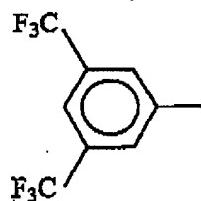


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characterised in that each of R^1 and R^2 independently comprises an alkyl, alkaryl or aryl group or a substituted derivative thereof, and contains at least one fluorine atom, and in that each of R^3 and R^4 is selected from the group which consists of H, alkyl, alkaryl and aryl and substituted derivatives thereof, including fluorine-containing derivatives.

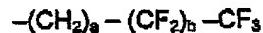
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2. A thiourea according to Claim 1 wherein R^1 is



15

3. A thiourea according to Claim 1 or 2 wherein R^2 is



20 wherein a is an integer not less than 1 and b is a whole number from 0 to 6.

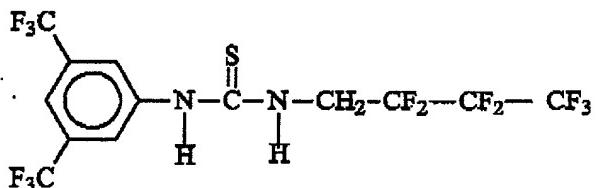
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4. A thiourea according to Claim 3 wherein R^2 is $-\text{CH}_2 - \text{CF}_2 - \text{CF}_2 - \text{CF}_3$.
5. A thiourea according to Claim 3 wherein R^2 is $-\text{CH}_2 - \text{CF}_3$.
6. A thiourea according to Claim 3 wherein b is 4, 5 or 6.

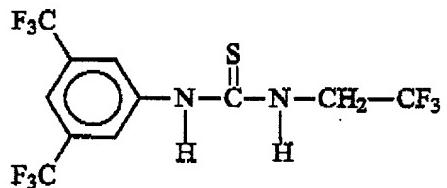
7. A thiourea according to any preceding claim wherein R³ is H.

8. A thiourea according to any preceding claim wherein R⁴ is H.

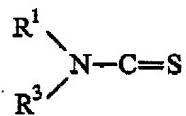
5 9. A thiourea according to Claims 2, 4, 7 and 8, viz. one of formula



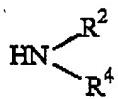
10 10. A thiourea according to Claims 2, 5, 7 and 8, viz. one of formula



11. A method of producing a substituted thiourea of the formula given and
15 defined in any preceding claim, characterised by reacting a compound of general
formula



with a compound of general formula



20 wherein R¹, R², R³ and R⁴ are as defined in any said claim.

12. A method of extracting a noble metal from a matrix, said method characterised by treating the matrix with a substituted thiourea according to any of Claims 1 to 10, and subjecting the thus treated matrix to supercritical fluid extraction.
- 5 13. A method according to Claim 12 wherein the noble metal is gold, platinum, silver, palladium or rhodium.
14. A method according to Claim 12 or 13 wherein the supercritical fluid is liquid carbon dioxide.
- 10 15. A method according to any of Claims 12 to 14 wherein the treatment with substituted thiourea is performed in the presence of an oxidant.
- 15 16. A method according to Claim 15 wherein the oxidant comprises ferric (Fe^{III}) ions.
17. A method according to any of Claims 12 to 16 wherein the treatment and extraction are carried out at room temperature and are followed by recrystallisation of the product from petroleum ether (100-120°).
- 20 18. Use of a thiourea according to any of Claims 1 to 10 in the extraction of gold, platinum, silver, palladium or rhodium from a matrix.

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; that I verily believe I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural names are listed below) of the subject matter claimed and for which a patent is sought in the application entitled:

"Complexing Agents"

U.S. Serial No. 09/890,967 Filed August 8, 2000

was filed as PCT International

~~International Application~~ Application No. PCT/IE 00/00018
filed February 8, 2000 and amended on

(for declaration not accompanying application)

that I have reviewed and understand the contents of the specification of the above-identified application, including the claims, as amended by any amendment referred to above; that I acknowledge my duty to disclose information of which I am aware which is material to the patentability of this application under 37 C.F.R. 1.56, that I hereby claim foreign priority benefits under Title 35, United States Code §119, §172 or §365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified on said list any foreign application for patent or inventor's certificate on this invention having a filing date before that of the application on which priority is claimed:

Application Number	Country	Filing Date	Priority Claimed (yes or no)
S99 0086	Ireland	February 8, 1999	Yes

I hereby claim the benefit of Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in a listed prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge my duty to disclose any information material to the patentability of this application under 37 C.F.R. 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status (patented, pending, abandoned)
28		

CANNED
 I hereby appoint John H. Mion, Reg. No. 18,879; Donald E. Zinn, Reg. No. 19,046; Thomas J. Macpeak, Reg. No. 19,292; Robert J. Seas, Jr., Reg. No. 21,092; Darryl Mexic, Reg. No. 23,063; Robert V. Sloan, Reg. No. 22,775; Peter D. Olexy, Reg. No. 24,513; J. Frank Osha, Reg. No. 24,625; Waddell A. Biggar, Reg. No. 24,861; Robert G. McMorrow, Reg. No. 19,093; Louis Gubinsky, Reg. No. 24,835; Neil B. Siegel, Reg. No. 25,200; David J. Cushing, Reg. No. 28,703; John R. Inge, Reg. No. 26,916; Joseph J. Ruch, Jr., Reg. No. 26,577; Sheldon I. Landsman, Reg. No. 23,430; Richard C. Turner, Reg. No. 29,710; Howard L. Berenstein, Reg. No. 25,665; Alan J. Kasper, Reg. No. 25,426; Kenneth J. Burchfiel, Reg. No. 31,333; Gordon Kit, Reg. No. 30,764; Susan J. Mack, Reg. No. 30,931; Frank L. Bernstein, Reg. No. 31,484; Mark Boland, Reg. No. 32,197; William H. Mandir, Reg. No. 32,156; Scott M. Daniels, Reg. No. 32,562; Brian W. Hannon, Reg. No. 32,778 and Abraham J. Rosner, Reg. No. 33,276, my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and request that all correspondence about the application be addressed to **SUGHRUE, MION, ZINN, MACPEAK & SEAS, 2100 Pennsylvania Avenue, N.W., Washington, D.C. 20037-3202.**

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date 25th February 2002

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2-01
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Fifth Inventor _____

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Citizenship _____

Date _____

Sixth Inventor _____

First Name

Middle initial

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Residence _____

Signature _____

Post Office Address _____

Citizenship _____

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Seventh Inventor _____

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Practitioner's Docket No. Q65804 09/890,967

**ADDED PAGE TO COMBINED DECLARATION AND POWER OF
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OR LEGAL REPRESENTATIVE ON BEHALF OF DECEASED OR
INCAPACITATED INVENTOR (37 CFR 1.42 AND 1.43)**

3-11

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hereby declare that I am a citizen of Ireland residing at 10 Broadford Cresc., Ballinteer, Dublin 16 IEX

and that I am executing and signing the declaration to which this is attached as

(check one):

- the administrator(trix) of
 executor(trix) of the last will and testament of
 legal representative (or heirs) of
Stephen John Harris

Full name of (first, second etc.) deceased or incapacitated inventor

British

Country of citizenship of deceased or incapacitated inventor

Ireland

Residence of deceased or incapacitated inventor

10 Broadford Cresc., Ballinteer, Dublin 16

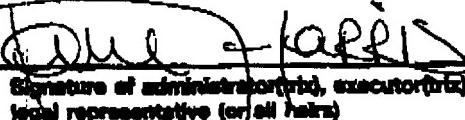
Post Office Address of deceased or incapacitated inventor

SAME

NOTE: The name of the first, second etc. deceased or incapacitated inventor should preferably also be filled in at the appropriate prior space of the declaration adding the words "deceased-completed on added page" or "incapacitated-completed on added page."

That, upon information and belief, I aver those facts that the Inventor is required to state.

Date: March 7, 2002


Signature of administrator(trix), executor(trix)
legal representative (or all heirs)

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